



## Gas-phase and catalytic combustion in heat-recirculating burners

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### Abstract

An experimental study of a spiral counterflow “Swiss roll” burner was conducted, with emphasis on the determination of extinction limits and comparison of results with and without bare-metal Pt catalyst. A wide range of Reynolds numbers ( $Re$ ) were tested using propane-air mixtures. Both lean and rich extinction limits were extended with the catalyst, though rich limits were extended much further. With the catalyst, combustion could be sustained at  $Re$  as low as 1.2 with peak temperatures as low as 350 K. A heat transfer parameter characterizing the thermal performance of both gas-phase and catalytic combustion at all  $Re$  was identified. At low  $Re$ , the “lean” extinction limit was actually rich of stoichiometric, and rich-limit had equivalence ratios exceeded 40 in some cases. No corresponding behavior was observed without the catalyst. Gas-phase combustion, in general, occurred in a “flameless” mode near the burner center. With or without catalyst, for sufficiently robust conditions (high  $Re$ , near-stoichiometric) not requiring heat recirculation, a visible flame would propagate out of the center, but this flame could only be re-centered if the catalyst were present. Gas chromatography indicated that at low  $Re$ , even in extremely rich mixtures, CO and non-propane hydrocarbons did not form. For higher  $Re$ , where both gas-phase and catalytic combustion could occur, catalytic limits were slightly broader but had much lower limit temperatures. At sufficiently high  $Re$ , catalytic and gas-phase limits merged. It is concluded that combustion at low  $Re$  in heat-recirculating burners greatly benefits from catalytic combustion with the proper choice of mixtures that are different from those preferred for gas-phase combustion. In particular, the importance of providing a reducing environment for the catalyst to enhance O<sub>2</sub> desorption, especially at low  $Re$  where heat losses are severe thus peak temperatures are low, is noted.

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### 1. Introduction

It is well known that hydrocarbon fuels contain 100 times more energy per unit mass than lithium-ion batteries, thus devices converting fuel to electricity at better than 1% efficiency represent improvements in portable electronic devices and other battery-powered equipment [1]. At small scales, however, heat and friction losses become more significant, thus devices based on existing

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macro-scale systems such as internal combustion engines may be impractical. Consequently, many groups have considered heat-recirculating, or “excess enthalpy,” burners [2,3] for thermal management and thermoelectric, piezoelectric or pyroelectric devices having no moving parts for power generation. In heat-recirculating burners, by transferring thermal energy from the combustion products to the reactants without mass transfer (thus dilution of reactants), the total reactant enthalpy (sum of thermal and chemical enthalpies) can be higher than that of the incoming cold reactants and therefore combustion under conditions (lean mixtures, low heating value fuels, and large heat losses) that would result in extinction without recirculation can be sustained.

At smaller scales, heat losses become more important due to increased surface area to volume ratios. A potential means of reducing the impact of these losses is to employ catalytic combustion, which may allow self-sustaining reaction to occur at lower temperatures, and thus higher heat losses than could be sustained with gas-phase combustion. The higher surface area-to-volume ratio at small scales makes area-limited catalytic combustion even more attractive compared to volume-limited gas-phase combustion. Additionally, since chemical reactions only occur on the catalyst surface, the heat source location is fixed. This makes heat transfer design simpler than for gas-phase combustion in which the reaction zone location may change in undesirable ways. Moreover, the lower temperature of catalytic combustion makes thermal stresses and materials limitations less problematic.

While extinction limits of heat-recirculating burners have been previously studied [2,3], only one study [4] examines catalytic combustion and only for hydrogen fuel. This is qualitatively different than the catalytic reaction of hydrocarbon fuels because with hydrogen, combustion on Pt can occur even at room temperature. Moreover, extinction limits were not reported in [4], and only external surface temperatures were measured. Consequently, the objectives of this work were to examine the extinction limits and temperature characteristics of heat-recirculating combustors with catalytic and non-catalytic (gas-phase) combustion of a hydrocarbon fuel over a large range of Reynolds numbers.

## 2. Experimental apparatus

A 3.5-turn square spiral counterflow Swiss roll burner (Fig. 1) was constructed by bending sheets of 0.5-mm thick inconel-718 alloy (thermal conductivity  $k \approx 11 \text{ W/m K}$  at 300 K) into a  $7 \text{ cm} \times 7 \text{ cm} \times 5 \text{ cm}$  tall burner. Each inlet and exhaust channel is 3.5 mm wide. The Rayleigh number based on channel width is less than 250 for all

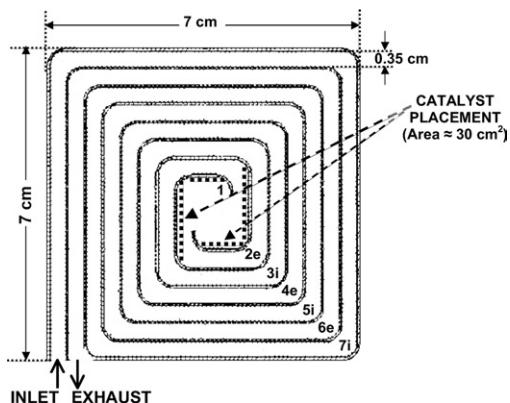


Fig. 1. Schematic plan view of the Swiss roll burner. Platinum catalyst strips were placed as shown when used. Thermocouples 1–7 were located in the exhaust ‘e’ and inlet ‘i’ turns as indicated.

gas temperatures, thus buoyancy effects on flow inside the channels are negligible. The burner top and bottom are sealed with 6 mm of fibrous ceramic blanket, backed by aluminum plates. For catalyst experiments, strips of bare platinum foil were placed along the walls in the central section of the burner (exposed area  $\approx 30 \text{ cm}^2$ ). An electrically heated Kanthal wire placed in the central region of the Swiss roll was used for ignition. The burner was instrumented with thermocouples located in its center, and in each inlet and exhaust turn (seven total, see Fig. 1). A separate set of experiments was performed with five thermocouples evenly spaced across the center section. Each thermocouple was supported by a 1-mm diameter alumina tube with only its bead protruding from the top of the tube. Temperature measurements are repeatable to  $\pm 20 \text{ K}$ . Commercial electronic mass flow controllers regulated the flow rate of fuel (propane), air, and where appropriate, diluent or reducing agent, into a mixing chamber and then into the outermost turn of the burner. LabView software recorded the thermocouple data and controlled the mass flow controllers. Extinction limits are repeatable to within 5% of the reported values. Gas samples were extracted from the exhaust using a syringe and analyzed using an SRI Instruments 8610C gas chromatograph with FID and TCD detectors. The GC was calibrated using both commercial calibration gases and the flow control system; agreement between the two calibrations was excellent. GC samples were extracted from each exhaust turn of the burner under fuel rich conditions to check for gas leakage through the fibrous ceramic blanket. No significant difference between measured oxygen concentrations in each turn was found, indicating that leakage between inlet and exhaust channels through the blanket is insignificant.

While bare metal Pt catalyst is unsuitable for practical applications, it was used because it is a readily available standard material and was found to yield very reproducible results. Catalyst performance degraded slightly over operating periods of the order of one week; simply polishing the foil restored catalyst performance. As demonstrated below, performance at low  $Re$  was markedly enhanced by treating the catalyst surface by burning propane-air mixtures with  $\approx 5\%$  of the propane replaced by ammonia, a strong reducing agent, for one hour; this enhancement would last for several days of operation. Reduction using rich propane-air or hydrogen-air yielded no similar conditioning benefit. Due to its low heating value, ammonia was found to have poor extinction limit performance, thus results with ammonia as a primary fuel are not reported here.

### 3. Results and discussion

#### 3.1. Extinction limits

Lean and rich extinction limits were determined by starting from a steady burning state and decreasing or increasing the fuel concentration until steady-state operation ceased and burner temperatures decayed to ambient. These limits were independent of the path in mixture-Reynolds number space used to reach the limit. Figure 2 shows extinction limits for a three-decade range of Reynolds numbers, defined based on the area-averaged *inlet* gas velocity ( $U$ ), gas kinematic viscosity at *ambient* conditions, and channel width (3.5 mm). At the highest  $Re$  studied ( $\approx 2000$ ), weakly turbulent flow is expected *near the inlet*. As gas temperature increases, gas velocity increases proportionally due to decreasing gas density, however, viscosity increases as  $T^{1.7}$ , thus  $Re$  decreases to  $\approx 700$  at the burner center, meaning

very weak if any turbulence exists there. Four sets of curves are shown in Fig. 2, indicating lean and rich extinction limits for catalytic combustion, gas-phase combustion, and boundaries of the “out-of-center reaction zone” regime discussed below, and extinction limits obtained with  $\text{NH}_3$ -conditioned catalyst.

Figure 2 shows two extinction regimes, one at high  $Re$  where the extinction limit equivalence ratio ( $\phi_{\text{lim}}$ ) increases slightly as  $Re$  increases, and one at low  $Re$  where ( $\phi_{\text{lim}}$ ) increases considerably as  $Re$  decreases. As shown previously [5–8], these limits correspond to finite residence time “blow-off” limits and heat loss induced limits, respectively. The heat-loss limit, which applies to most of our test conditions, results because (as we will show) peak temperatures are only weakly dependent on  $Re$ , thus heat loss rates are almost independent of  $Re$ . In contrast, heat generation rates are proportional to mass flow and thus  $Re$ . Consequently, lower  $Re$  leads to larger ratios of heat loss to heat generation rates; extinction results when this ratio increases to values near unity. At  $Re = 980$ , corresponding to mixture inlet velocities 10 times the *stoichiometric* laminar burning velocity,  $\phi_{\text{lim}} \approx 0.18$  compared to  $\phi_{\text{lim}} \approx 0.51$  for conventional propane-air flames. Thus, as shown previously [2,3], heat-recirculating burners can greatly augment combustion rates. Weinberg's data [2] are not shown in Fig. 2 because no extinction limits at  $Re < 500$  were reported and because methane rather than propane fuel was used.

Figure 2 shows that lean limits are extended slightly and rich limits are extended drastically using the catalyst. Gas-phase combustion could not be sustained at  $Re < 40$ , whereas with catalyst, combustion could be sustained at  $Re \approx 1$ . For  $Re < 15$ , the *lean* catalytic extinction limit is actually *rich* of stoichiometric. Also, rich limits could be extremely rich, for example  $\phi_{\text{lim}} > 40$  for  $Re = 15$ . No similar trend was found without catalyst; non-catalytic limits were nearly symmetric about stoichiometric. Figure 2 also shows that catalyst reduction using ammonia (see Experimental Apparatus) significantly improves the catalyst performance, but only for  $Re < 30$ , corresponding to conditions with low maximum temperatures (due to heat losses) and long residence times.

At high  $Re$ , catalytic and gas-phase extinction limits converge, thus catalysis is ineffective compared to gas-phase combustion. This is probably because laminar flow prevails, thus the Sherwood number is constant; consequently mass transfer to the catalyst does not increase as  $Re$  (and therefore reactant mass flow) increases, meaning that at sufficiently high  $Re$  the ratio of mass flux to the catalyst to the total mass flux becomes very small and only a small fraction of the fuel can be burned catalytically.

The standard practice of changing fuel-air equivalence ratio changes two important parameters:

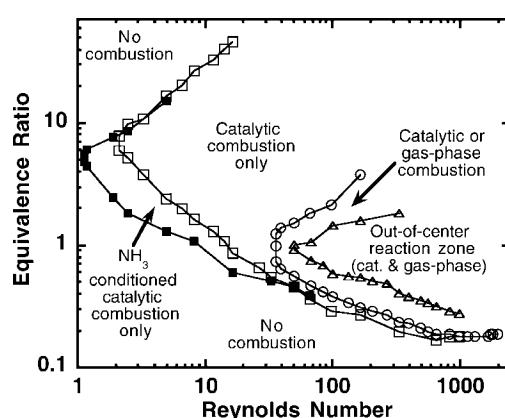


Fig. 2. Extinction limit map for catalytic and gas-phase combustion in the inconel Swiss roll.

ters simultaneously: fuel-to-oxygen ratio and adiabatic flame temperature. For gas-phase combustion, the latter has far more influence on combustion properties, and thus lean-limit and rich-limit properties are fairly symmetrical about  $\phi = 1$ . However, catalytic combustion limits are highly nonsymmetrical. With this motivation, experiments were performed to test fuel-to-oxygen ratio and adiabatic flame temperature effects independently by fixing the fuel-to-oxygen ratio and increasing nitrogen dilution until extinction took place. Figure 3 shows distinct differences in behavior for catalytic and gas-phase combustion with this strategy. For gas-phase combustion, the fuel concentration at extinction is nearly constant lean of stoichiometric and increases roughly linearly with fuel-to-oxygen ratios rich of stoichiometric (since oxygen is the limiting reactant in this case). Maximum burner temperatures at the extinction limits are relatively constant. For catalytic combustion, a step decrease in both fuel concentration at extinction and limit temperature occurs as the fuel-to-oxygen ratio crosses stoichiometric. For rich fuel-to-oxygen ratios, the limiting fuel concentration is nearly constant—*even though oxygen, not fuel, is the limiting reactant*—meaning the mixture is becoming more oxygen-deficient as fuel-to-oxygen ratio increases. Benefits of rich operation have also been noted for methane fuel in microscale *isothermal* reactors [9].

It is proposed that the effects of fuel-to-oxygen ratio on catalytic combustion are due to adsorption of oxygen as O(s) on Pt. As shown previously [8,10], at low temperatures, O(s) coverage on Pt is nearly complete, thus fuel cannot reach the catalyst surface. Under these conditions, excess fuel is required to prevent O(s) coverage of the platinum catalyst surface. Under rich conditions, ex-

cess gas-phase oxygen is not present, and CO(s) dominates surface coverage. At our low reaction temperatures, CO(s) is a much less effective barrier to C<sub>3</sub>H<sub>8</sub> adsorption than O(s).

For some tests, a Pyrex window was used in place of the aluminum top plate. These tests showed that over the majority of conditions shown in Fig. 2, in particular whenever combustion was centered (with or without catalyst), combustion occurred in a “flameless” mode where no visible emission could be observed, even in a darkened room. Flameless combustion has also been observed in other systems, for example nonpremixed counterflow configurations of fuel and highly preheated air [11–13]. Flameless combustion is, in general, characterized by much broader reaction zones than conventional premixed flames. Other investigators [14,15] have reported flame broadening for premixed flames in narrow channels with heat recirculation through or across channel walls. Broad reaction zones are probably ubiquitous in heat-recirculating burners because under conditions where combustion requires excess enthalpy via heat recirculation for its survival, heat transfer to the reactants occurs on the scale of the channel width. This makes it difficult to sustain the large gradients associated with conventional propagating premixed flames (length scales much smaller than our channel width). Combustion in heat-recirculating burners is probably more similar to plug-flow reactors, which are employed specifically to broaden reaction zones compared to flames. Consistent with this notion, our maximum temperatures are akin to flow reactor temperatures and almost always below those of conventional flames (see next section). The key difference is that in flow reactors the temperature-time profile is prescribed via electrical heaters and dilute mixtures are used to minimize heat release, whereas in heat-recirculating burners the profile is inherently coupled to heat release. Although detailed measurements of reaction zone thickness were not performed, experiments were performed to determine temperature uniformity in the burner central region as described in the next section.

The region in Fig. 2 labeled “out-of-center reaction zone” corresponds to higher Reynolds numbers where the ratio of heat loss to heat generation is lower and to near-stoichiometric mixtures that are strong enough to yield propagating fronts without the benefit of heat recirculation. Under these conditions, visible flames stabilized near the burner inlet were observed. (This is a “flashback” limit with respect to the burner center but the flame can still exist within the burner.) The out-of-center limit was the same for catalytic and gas-phase combustion, which is expected since the catalyst should have no significant effect (in terms of heat release) on the combustion products of a flame upstream of

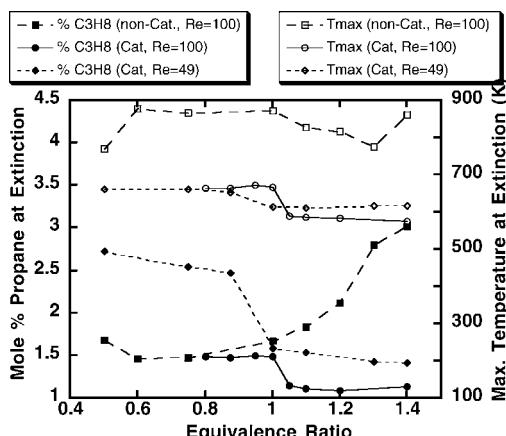


Fig. 3. Fuel concentration and maximum measured burner temperatures at extinction limit conditions obtained by fixing the fuel to oxygen ratio and diluting with nitrogen.

the catalyst. Nevertheless, we observed an important difference between catalytic and non-catalytic out-of-center limits, once a gas-phase reaction moved out-of-center, it could not be re-centered by re-adjusting the mixture to weaker (farther from stoichiometric) compositions, whereas catalytic reaction could easily be re-centered. This is plausible since the region downstream of the flame is cooler than that near the gaseous flame, and catalytic extinction limit temperatures are much lower than that for gas-phase combustion (see next section). Thus for the catalytic case only, the burner center conditions are suitable for re-stabilization once the out-of-center flame retreats from the inlet towards the center.

### 3.2. Thermal behavior

Figure 4 shows the maximum temperatures recorded in the burner ( $T_{\max}$ ) at the extinction limit as a function of  $Re$  for both gas-phase and catalytic combustion. All cases shown correspond to centered combustion (temperature at TC1 larger than all other measurement stations). Temperature profiles across the burner (discussed below) show that TC1 is very indicative of the true temperature maximum, especially for catalytic combustion.

Perhaps, the most noteworthy aspect of Fig. 4 is the low temperature capable of sustaining combustion with catalyst. The minimum temperature observed is 350 K at  $Re = 1.2$ , corresponding to  $U = 0.5$  cm/s. Even at  $Re = 650$  ( $U = 280$  cm/s), combustion could be sustained at 750 K. For both catalytic and gas-phase reactions, the minimum temperature required to support combustion increases as  $Re$  increases. This is expected since higher  $Re$  means higher velocities (since neither channel width nor viscosity was changed), thus shorter residence times, and consequently a faster

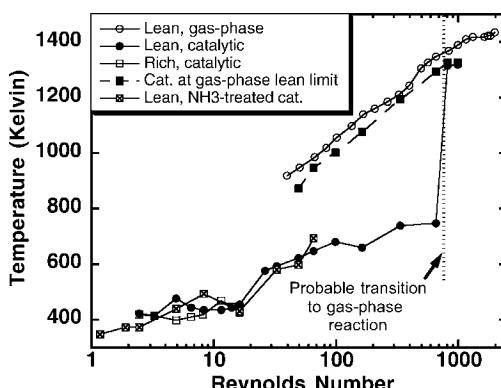


Fig. 4. Maximum burner temperatures ( $T_{\max}$ ) at the extinction limits. All data shown correspond to centered combustion (see Fig. 2).

reaction required to sustain combustion. Faster reaction, in turn, requires higher temperatures. In fact, Fig. 4 can be redrawn as an Arrhenius plot ( $\ln(Re)$  vs.  $1/T_{\max}$ ). The resulting plot (not shown) is nearly linear with slopes corresponding to effective activation energies ( $E$ ) of about 19 and 6.4 kcal/mol for gas-phase and catalytic limits, respectively. At first glance, the latter seems rather low, but the dimensionless activation energy ( $E/RT_{\max}$ ) for the  $Re = 1.2$  limit case is 9.2, indicating significant sensitivity to temperature.

Minimum temperatures required to support combustion with catalyst are 300–500 K less than for gas-phase reaction, though the difference in limit mixture compositions is small (Fig. 2). For this reason, an additional curve is given in Fig. 4 that shows  $T_{\max}$  at the limit with catalytic reaction for the mixture at the gas-phase lean extinction limit. The catalytic temperatures are slightly lower than with gas-phase reaction only. This suggests that under these conditions, the catalyst is actually slightly detrimental; for our system, catalytic reaction is beneficial only when gas-phase reaction is not possible.

For  $Re > 750$ , gas-phase and catalytic temperatures converge. This  $Re$  corresponds to the convergence of lean extinction limits (Fig. 2). It is noteworthy that even without catalyst and at high  $Re$ , the temperatures required to support combustion ( $\approx 1100$  K) are lower than for propagating hydrocarbon–air flames (1500 K), again indicating conditions more similar to plug-flow reactors than flames.

Figure 5 shows temperatures at all 7 thermocouples for the entire range of mixture compositions at  $Re = 100$  that sustain catalytic combustion. For sufficiently lean or rich mixtures, the reaction is centered, thus TC1 recording the highest temperature ( $T_{\max}$ ). For mixtures near

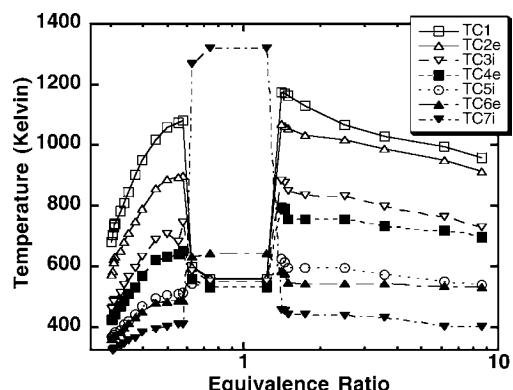


Fig. 5. Temperature profiles recorded over a range of mixture compositions for catalytic combustion at  $Re = 100$  with catalyst. Lean and rich gas-phase extinction limits are 1.55% and 8.25% fuel ( $\phi = 0.39$  and  $\phi = 2.05$ ).

stoichiometric, however, the reaction zone moves upstream and stabilizes in the first inlet turn. For these mixtures, TC7<sub>i</sub>, located in the outermost inlet turn, records the highest temperature and the burner interior acts as a heat sink. This transition in thermal behavior corresponded exactly to the transition from flameless combustion to visible flaming combustion in the inlet turns of the burner.

To determine the temperature uniformity in the burner center, tests were performed with five thermocouples, designated TC8–TC12, spanning this region (see Experimental apparatus) for a wide range of  $Re$  at fixed fuel concentration. The outermost thermocouples, TC8 and TC12, were placed 0.5 mm from the catalyst surface (corresponding to the radius of the ceramic tube used to isolate each thermocouple) to prevent electrical short circuiting. 2% fuel was chosen for non-catalytic and 20% for catalytic cases because these mixtures provided centered combustion over relatively wide ranges of  $Re$ . Figure 6 shows the recorded temperatures and the statistic  $\sigma/T_{\text{avg}}$ , where  $\sigma$  is the standard deviation and  $T_{\text{avg}}$  is the average of TC8–TC12. For the catalytic case,  $\sigma/T_{\text{avg}} < 0.03$  for all  $Re$ , indicating highly uniform

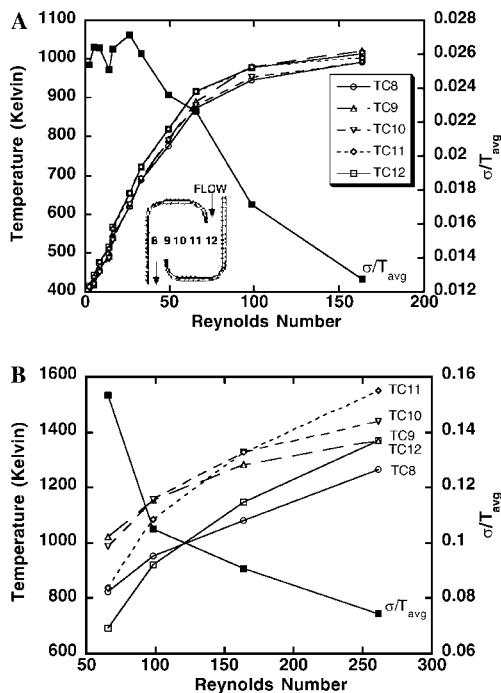


Fig. 6. Center temperature profiles for (A) catalytic reaction with 20%  $\text{C}_3\text{H}_8$  in air ( $\phi = 4.98$ ) and (B) lean gas-phase reaction with 2%  $\text{C}_3\text{H}_8$  in air ( $\phi = 0.50$ ).  $T_{\text{avg}}$  is the average temperature recorded by thermocouples TC8 through TC12 and  $\sigma$  is the standard deviation of these temperatures at a given  $Re$ . Thermocouple placement is shown in (A).

center temperatures though temperatures are marginally higher near the catalyst surface (TC8 and TC12), where the reaction occurs.  $\sigma/T_{\text{avg}}$  is higher for gas-phase combustion, though still less than 0.1 for  $Re \geq 100$ . For gas-phase combustion, the temperature is higher in the center (TC9–11) than near the walls since gas-phase reaction may occur throughout the center and heat is transferred to the walls.

As discussed in Section 1, heat-recirculating burners transfer heat from the combustion products to the reactants and thereby increase the reactant total enthalpy. Consequently, heat transfer and excess enthalpy should be related. The total heat recirculation should be proportional to the difference between the temperature of each outlet turn ( $T_o$ ) and each inlet turn ( $T_i$ ) adjacent to that outlet turn. With this motivation, a dimensionless heat transfer parameter ( $Q$ ) defined as  $[\sum(T_o - T_i)]/T_{\infty}$ , where  $T_{\infty}$  is ambient temperature, was defined. In principle, the differing areas of each turn should be considered, but each successive turn inward is hotter, thus thermal conductivity is higher, which offsets the area effect to some extent. Figure 7 shows the correlation between  $Q$  and dimensionless excess enthalpy ( $H$ ) defined as  $(T_{\text{max}} - T_{\text{ad}})/(T_{\text{ad}} - T_{\infty})$ , where  $T_{\text{ad}}$  is the adiabatic flame temperature, for all limit conditions.  $H$  is well correlated with  $Q$  for both catalytic and gas-phase combustion.  $H$  of course increases with  $Q$  but not linearly due to the impact of heat losses at low  $Q$ . Note that at low  $Q$ , corresponding to low  $Re$ ,  $H$  can be negative, indicating self-sustaining combustion at highly sub-adiabatic temperatures, even with heat recirculation. Such low- $Re$  behavior has been predicted theoretically [6]. Nevertheless, the benefit of heat recirculation is substantial, allowing combustion at very low thermal power. At  $Re = 1.2$ , the heat release rate (assuming complete consumption of the deficient reactant) is less than 3 W—about 20 times less

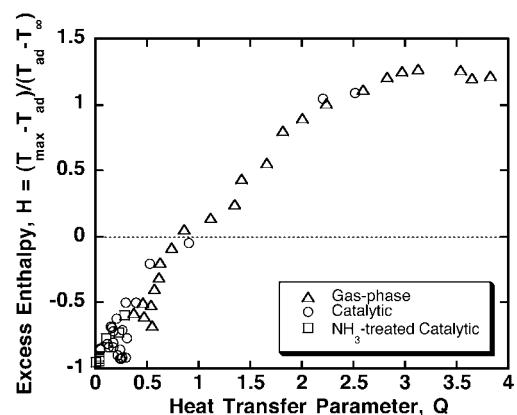


Fig. 7. Correlation of excess enthalpy ( $H$ ) with heat transfer parameter ( $Q$ ) for all extinction limit conditions.

Table 1

Exhaust gas chromatography measurements for both catalytic and gas-phase combustion over a range of Reynolds numbers. X = not detected

Re	Combustion mode	Catalyst area (cm <sup>2</sup> )	Percent (molar basis)					% C <sub>3</sub> H <sub>8</sub> Conversion
			[C <sub>3</sub> H <sub>8</sub> ] <sub>inlet</sub> (Φ)	[C <sub>3</sub> H <sub>8</sub> ]	[CO <sub>2</sub> ]	[CO]	[HC] <sup>a</sup>	
10	Catalytic	30	6.26 (1.56)	2.69	10.7	X	X	57.0
	Catalytic	120	6.17 (1.54)	2.40	11.3	X	X	61.1
	Catalytic	30	35.0 (8.72)	33.3	5.21	X	X	4.86
	Catalytic	120	35.3 (8.78)	33.2	6.27	X	X	5.95
16	Catalytic	30	4.03 (1.00)	0.822	9.63	X	X	79.6
	Catalytic w/NH <sub>3</sub> treatment	30	4.08 (1.01)	0.108	11.9	X	X	97.4
33	Catalytic	30	3.26 (0.81)	0.42	8.53	X	X	87.1
		120	3.14 (0.78)	0.237	8.70	X	X	92.5
100	Catalytic	30	1.81 (0.45)	0.332	4.44	X	X	81.7
		30	7.57 (1.88)	3.66	8.29	2.54	0.520	51.7
	Gas-phase	n/a	1.83 (0.46)	X	5.50	X	X	100
		n/a	7.84 (1.95)	3.60	4.02	7.79	0.704	54.1
1000	Catalytic	30	10.8 (2.68)	6.64	5.71	3.33	1.75	38.5
	Gas-phase	n/a	10.8 (2.68)	6.47	5.92	3.36	2.08	40.1

<sup>a</sup> Includes all detected hydrocarbons except C<sub>3</sub>H<sub>8</sub>.

than a common candle (though of course smaller burners than that used here are more appropriate for small thermal powers).

### 3.3. Exhaust gas analysis

Table 1 shows the results of exhaust gas analysis. For catalytic reaction at  $Re = 10$  (no gas-phase reaction occurs at  $Re = 10$ , see Fig. 2), the exhaust contains mostly unburned fuel and carbon dioxide. No carbon monoxide or unburned (non-C<sub>3</sub>H<sub>8</sub>) hydrocarbons are present, for either the lean-limit or rich-limit mixture, even though the latter contains 35% fuel, and even though calibration samples containing 0.01% CO and hydrocarbons could be detected. H<sub>2</sub> was not detected, thus presumably all fuel-bound H that reacted formed water. When NH<sub>3</sub>-conditioned catalyst is used at low- $Re$  conditions where the benefit of conditioning is greatest (Fig. 2), fuel conversion increased significantly. For an intermediate case,  $Re = 100$ , for lean conditions no CO or non-C<sub>3</sub>H<sub>8</sub> hydrocarbons were detected for either catalytic or gas-phase reaction, but catalytic reaction results in slightly less fuel consumption. For rich conditions, catalytic reaction again results in lower fuel conversion than gas-phase reaction; however, there is more complete conversion of CO to CO<sub>2</sub> and fewer non-C<sub>3</sub>H<sub>8</sub> hydrocarbons. For  $Re = 1000$ , gas-phase reaction dominates (see Figs. 2 and 4); results with and without catalyst are similar.

As noted previously, nominally 30 cm<sup>2</sup> of catalyst was employed. Additional tests were performed spreading this 30 cm<sup>2</sup> over twice the

nominal burner area, invading both the center, and adjacent inlet and exhaust turns. Extinction limits and exhaust products were nearly identical to the baseline catalyst arrangement. Other tests were performed using 120 cm<sup>2</sup> of catalyst in the burner center. Again, extinction limits were only slightly changed, and Table 1 shows that this case resulted in only modestly greater fuel conversion.

These results suggest catalytic extinction at low  $Re$  is not due to insufficient catalyst area or insufficient residence time (since complete conversion of reacted fuel was found) but rather by the need to maintain sufficient surface sites not covered by O(s), which, in turn, is more difficult at lower  $Re$  due to the greater impact of heat losses, and thus lower maximum attainable temperatures, which makes O(s) desorption more difficult.

### 4. Conclusions

Experiments were conducted in a heat-recirculating burner with and without platinum catalyst over a wide range of Reynolds numbers, particularly low  $Re$  characteristic of micro-scale combustion devices.  $Re$  effects dominate combustor performance, even at low  $Re$  where laminar flow prevails, because low flow rates correspond to larger ratios of heat loss to heat generation, and thus lower peak temperatures. Since effective activation energies indicate that reaction rates are sensitive to temperature, even for catalytic combustion, sufficiently low  $Re$  do not support combustion. With a catalyst, however, because of the much lower effective activation energy, combustion could be sup-

ported at much lower  $Re$  (minimum  $\approx 1$  vs.  $\approx 40$  without catalyst for our burner) and at extremely low temperatures ( $\approx 350$  K vs.  $\approx 920$  K).

Combustor performance was very different with and without the catalyst. Without catalyst, extinction limits and maximum temperatures were nearly symmetric with respect to stoichiometric since stoichiometric conditions yield the highest potential flame temperatures. With catalyst, an additional driving force was the need to desorb O(s) via rich mixtures, thus behavior was very biased toward richer mixtures (rich fuel-air mixtures or rich fuel–O<sub>2</sub> mixtures diluted with N<sub>2</sub>). This led to *lean* limits *rich* of stoichiometric with extraordinarily rich ( $\phi_{\text{lim}} > 40$ ) limits. Even for such rich conditions, CO and non-C<sub>3</sub>H<sub>8</sub> hydrocarbon formation was negligible. As a result, extinction behavior with catalyst at low  $Re$  is similar at the lean and rich limits; for example, the extinction limit temperature is the same at the lean and rich catalytic limits for low  $Re$ , even though the mixtures are very different. Reconfiguring or increasing catalyst area had little effect on these limits, again indicating the need for O(s) desorption as opposed to increased transport or residence time. At higher  $Re$ , where either catalytic or gas-phase combustion is possible, the catalyst slightly degraded the performance, probably due to quenching of gas-phase radicals. The catalyst would enable slightly leaner mixtures to be burned, though at much lower temperatures and therefore much lower fuel utilization. CO and hydrocarbons do form for rich mixtures at moderate Reynolds numbers, but form less with the catalyst. At still higher  $Re$ , gas-phase combustion dominates, probably because of the limitation on mass transfer to the catalyst surface (since flows at the burner center are laminar, even at the highest  $Re$  tested).

It is undesirable to employ extremely rich mixtures due to poor fuel utilization. The tests with rich fuel–O<sub>2</sub> mixtures diluted with N<sub>2</sub> suggest that a viable alternative strategy might operate slightly rich of stoichiometric with exhaust gas dilution (rather than N<sub>2</sub> that would need to be carried with the fuel) to minimize oxygen coverage.

For conditions (very lean/rich mixtures and/or low  $Re$ ) where the mixture is too weak to sustain combustion without heat recirculation, the reaction zone must be located near the burner center, where the maximum heat recirculation occurs. Under these conditions, a “flameless” mode of combustion was prevalent, even without catalyst. Of course, heat recirculation is not always required for stable combustion. For conditions where combustion is self-sustaining without heat recirculation, a more conventional visible flame propagates out of the burner center toward the inlet; the rest of the burner acts as a heat sink. The out-of-center limits are the same with or without a catalyst. Without catalyst, decreasing the mixture

strength causes the flame to be blown back past the center and extinguish. With the catalyst in place, since catalytic limit temperatures are much lower than gas-phase limit temperatures, combustion can be re-established in the center.

Future work will include testing other fuel/catalyst combinations, as well as the effect of wall thickness and thermal conductivity on burner performance; thickness and conductivity have recently been identified as key factors in low- $Re$  performance [6,7]. Additionally, Reynolds number is not the only parameter needed to characterize combustor operation. In particular, our use of a fixed burner size implies that residence time (thus Damköhler number ( $Da$ ), the ratio of residence to chemical time scales) and  $Re$  could not be adjusted independently. To remedy this situation, in future work we will test geometrically similar burners of different physical sizes, with the aim of determining independently the effects of  $Re$  and  $Da$ , and thereby identify optimal operating conditions for microscale burners.

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## Comments

*Ajay K. Agrawal, University of Oklahoma, USA.* This is a generic question referring to the terminology of meso/microscale combustion. While the dimensions of your combustor are on the order of a few millimeters (and hence, meso-scale), the overall system size including the swiss-roll heat exchanger is much greater. Since swiss-roll is integral to your burner, should it not be included in sizing the combustor, which would then hardly be meso-scale?

*Reply.* We propose the following definition of “microscale” combustion, which is certainly not the only possible one: microcombustion occurs in flames whose physics is qualitatively different from conventional flames used in macroscopic power generation devices, specifically (1) the Reynolds numbers are too small for turbulent flow to occur, thus the benefits of acceleration of mixing, heat transfer and flame wrinkling by turbulence are absent; and (2) the channel dimension is smaller than the quenching distance, thus some additional measure (heat recirculation, catalytic combustion, reactant preheating, etc.) is needed to sustain combustion. By this definition most of our test conditions were in the “microcombustion” regime. Your point is well taken, however, in that if condition (2) were based on the overall device dimension, then only operation with mixtures for which combustion cannot be sustained at all without heat recirculation (i.e., conventionally non-flammable mixtures, infinite quenching distance) would qualify for “microcombustion” status.

roll) a mixture that was too rich to burn in the gas-phase but could still burn catalytically. This would sustain reaction until fresh incoming mixture reached the catalyst again, followed by another flashback and so on, leading to a “catalytic pulsed combustor” mode of operation.

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*Dimitrios C. Kyritsis, University Illinois at Urbana-Champaign, USA.* Your ability to burn a very rich mixture and end up with  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and the parent fuel as dominant products is remarkable! Would you offer an insight as to the chemical mechanisms that would lead to this?

*Reply.* The behavior you mentioned occurs only with catalytic combustion, which has a very important distinction from gas-phase combustion. In gas-phase combustion, temperature plays the key role in determining reaction rates; fuel-to-oxygen ratio is secondary. In catalytic combustion, adsorbed oxygen,  $\text{O}(\text{s})$ , is the dominant surface species and must be desorbed in order for fuel to reach the surface and begin reaction. Thus, surface condition and hence reactant fuel-to-oxygen ratio are of critical importance in determining reaction rates. In our ultra-rich mixtures, the additional fuel drives the surface condition away from  $\text{O}(\text{s})$ . At the very low temperatures where the ultra-rich mixtures sustain combustion, there is no gas-phase reaction that might produce  $\text{CO}$  or non-fuel hydrocarbons. Fuel that reaches the surface as well as intermediates such as  $\text{CO}$  are relatively tightly bound to the surface, whereas  $\text{CO}_2$  and  $\text{H}_2\text{O}$  desorb much more readily—it is this property of platinum that makes it so useful as a combustion catalyst. Thus, the fuel that reaches the surface does not leave until it oxidizes to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Consequently, this combination of low temperatures that do not exhibit gas-phase combustion, plus the adsorption/desorption properties of hydrocarbon-air mixtures on Pt catalyst cause the unusual behavior of rich mixtures at low Reynolds numbers (corresponding to low temperatures.)

These points are discussed more fully in [8] of the written paper.

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*Dion Vlachos, University of Delaware, USA.* 1. The flammability limits being rich at low Reynolds number in the catalytic heat recirculation burner is a very interesting discovery. Do you know the underlying mechanism?

*Christopher Cadou, University of Maryland, USA.* Do you observe any instabilities associated with the catalyst and have you had problems with “burning out” the catalyst when you transition to high temperature gas-phase combustion at higher Reynolds number?

*Reply.* We did not perform a systematic study of changes in catalyst behavior over time, but anecdotally we found that the catalyst was fairly robust; we could operate for several weeks with little change in performance, after which polishing and (optionally) ammonia-treating the catalyst would restore it to its initial state. We did not notice “burn out” but generally we minimized the amount of time spent in the high temperature operation regime.

In terms of instabilities during operation, we did notice under slightly rich conditions corresponding to the “out of center” regime, a flashback could occur, leaving behind (in the inlet turns of the Swiss

2. How do you envision integrating such a burner into devices given the excess of fuel at the exhaust? For example, have you explored recycling at the small scale?

*Reply.* 1. Addressed in the response to Prof. Kyritsis's comment.

2. The excess fuel is certainly problematic for practical devices, but the good news is that unburned fuel is less problematic than CO or non-fuel hydrocarbons,

particularly if the fuel is a small paraffin such as propane. Nevertheless, we are considering means to reduce the unburned fuel emission, e.g., by “staging” the combustion process by bleeding in additional air along the catalyst as fuel is consumed to maintain a locally rich mixture. As you mention another possibility is exhaust gas recycling; this point was discussed in our prior work ([8] in paper). We hope to present results of such experiments in the near future.